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Thermally stimulated conductivity of CaS phosphors activated by Ce

Vijay Singh, Manoj Tiwari*[1], O N Awasthi, S J Dhoble[2], R N Dubey[3] and M S Qureshi[3]

Department of Physics, Regional Institute of Education, Bhopal-462 013, Madhya Pradesh, India

[1] Department of Physics, Bansal College of Engineering, Mandideep-462 046, Madhya Pradesh, India

[2] Department of Physics, Kamla Nehru College, Nagpur-440 009, Maharashtra, India

[3] Department of Physics, Mulana Azad National Institute of Technology, Bhopal-462 007, Madhya Pradesh, India

E-mail manojjiin@yahoo.co in

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bstract Thermally Stimulated Conductivity (TSC) study has been made on CaS Ce phosphors, prepared with different activator concentrations nergies of trap levels corresponding to peaks were calculated using three different methods Trap depths/activation energy, relaxation time anc tempts to escape frequency are evaluated The variation in the values of trap depths is studied for the observation of TSC of γ-irradiated phosphors

Keywords Thermally stimulated conductivity (TSC), doping, phosphors

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1. Introduction

Luminescence properties of alkaline earth sulphide phosphors are well known since the time of Pauli [1]. This class of phosphors again received considerable attention after the discovery of IR stimulation and sensitization. More and more investigations were carried out by many workers like Randall-Wilkins [2], Garlick-Gibson [3] and Apple-Williams [4]. Mott-Gurney [5] and others to understand the luminescence mechanism fully. Continued efforts are being made even today to understand the different aspects of the phenomenon. For this purpose, we select the CaS phosphors with Ce impurity for our study.

Thermally Stimulated Conductivity (TSC) and thermoluminescence (TL) have been widely used as tools for he determination of activation energy/trap depth, relaxation ime and attempts to escape frequency parameters in luminescent nd photo conducting materials, since they involve directly the hermal release of trapped carriers. Most of the methods [6-8] vailable for evaluating the activation energy and other arameters from TSC are based upon the electron kinetics. The echniques adopted in the thermally stimulated conductivity TSC) studies are direct consequences of the studies on glow eaks in thermoluminescence work. The authors have made a study of CaS phosphors activated by Ce.

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The basic equation adopted here to interpret the TSC of phosphors is the one derived by Randall and Wilkins [2]:

$$i(T) = A.\exp\left(\frac{-E}{KT}\right) - \frac{1}{\beta\tau_0}\int_{T_0}^{T}\exp\left(\frac{-E}{KT}\right)dT \qquad (1)$$

where A is a constant involving the product of charge mobility, free lifetime and depth of penetration of charges, E-the trap depth, K-the Boltzmann constant, T-the absolute temperature, β-the heating rate and τ_0 -the inverse of the trap escape frequency. The different parameters such as trap depth E, relaxation times τ_0, and attempt to escape frequency can be calculated using at least three different methods:

(i) Initial rise method :

According to Garlick and Gibson [3], the low temperature tail of eq.(1) is given by:

$$\ln i = C - \frac{E}{KT} \qquad (2)$$

Slope of ln $i(T)$ *vs* $1/T$ curve yields the value of E.

On differentiating eq. (1) to get the maximum value of current, one obtains

$$\tau_0 = \frac{KT_m^2}{\beta E \exp\left(\frac{E}{KT_m}\right)}. \qquad (3)$$

The time-constant for any other temperature can be obtained from the equation :

$$\tau = \tau_0 \exp\left(\frac{E}{KT}\right), \tag{4}$$

which gives only rough estimate of E and τ_0 .

(ii) Bucci plot method [8] :

This method is more accurate, because it utilises the whole TSC curve while in the former method, only a few points could be obtained, and gives better results. From eq. (4),

$$\ln \tau = \ln \tau_0 + \frac{E}{KT} . \tag{5}$$

But it can be shown that

$$= \int_{i(T)} \frac{i(t)}{i(T)}\, dt . \tag{6}$$

The integration of eq. (6) can be estimated with fairly good accuracy by graphical interpretation of the TSC curve. In this way, a number of values of $\tau(T)$ can be calculated at different temperatures.

From eq. (5), the slope of the straight line between $\ln\tau$ *vs* $1/T$ gives E/K while intercept on the $\ln(\tau)$ axis gives the value of $\ln(\tau_0)$.

(iii) Cowell and Woods' [9] Curve Fitting Method :

Substitution of $x = E/KT$ and $dx = (-E/KT^2)dT$ in eq.(1) and expansion give an approximate relation of TSC is as follow:

$$i(x) \approx A \exp\left[-x - B \exp(-x) x^{-2}\right]. \tag{7}$$

By differentiating eq.(7) and equating to zero, it is seen that the maximum of the curve occurs at $t = t^* = \beta/Kt_m$ and we have

$$B' = \frac{\exp x^* . x^{*3}}{x^* + 2} \tag{8}$$

where B' is an approximate value of B. The pair of eqs. (7) and (8) is used for the curve fitting technique. The value of T_{max} is obtained from the experimental curve of E. The methods described in (i) and (ii) are used to calculate an approximate value of E. With T_{max}, this leads to an approximate value of B'. Value of $i(t^*)$ is then calculated from eq.(7) using the approximate value of B' instead of B. A is used as an adjustable parameter to normalize the theoretical curve with the experimental one at the maximum, so that

$$A = \frac{i(x^*)}{\exp\left[-x^* - B' \exp(-x^*)\, x^{*-2}\right]} . \tag{9}$$

Any error in the initial value of E' chosen, is indicated by a failure to obtain a good fit between the two low temperature portions of the theoretical curve lying above the experimental curve while the reverse is true for a chosen value of E which is too high. A new value of E' chosen and the procedure is repeated until an excellent fit is obtained. The sensitivity of the method is such that about 2% change in E' causes an appreciable lack of fitting of the theoretical and the experimental curves.

Once the curves have been fitted and the final value of E has been determined, eq.(3) is used to calculate τ_0 and then $B = 1/\beta\tau_0$ gives the value of B. An advantage of Cowell and Woods methods is that the value of A can also be obtained from which one can get initial density of filled traps.

3. Experimental details

Phosphor Preparation :

CaS phosphors were obtained using solid-state reaction with cerium and $CaSO_4$ as starting materials and fired at higher temperature for two hours. The reducing agent was AR grade carbon powder and Na_2SO_4 as a flux used in synthesis. Amount of cerium was varied from 0.01 to 1.1 mole percent. The details of phosphor preparation are the same as reported in earlier paper [10].

TSC measurement:

To study TSC, pellets of 20 mg of phosphor samples, prepared by a pressing machine and sintered at about 100°C were used. All the samples were pressed to form pellets of 9 mm diameter and 1.5 mm thickness. Exposure to γ -ray was performed using a ^{60}Co source. The pellet of the test sample was put in a typical sample holder fabricated in this laboratory. The sample holder was kept inside a specially prepared and properly grounded programmable temperature controlled furnace. Pellets were heated each time at the rate of 5°C per second. The apparatus used for observing TSC was the same as described elsewhere [10-12].

4. Results and discussion

To study the effect of activator concentration on the behaviour of calcium sulphide phosphors, a series of samples were prepared. The Garlick-Gibson plot between ln (i) and $1/T$ for TSC curves plotted. In this initial rise method, only limited experimental poi are available, so the slope of the straight-line plot is quite ambiguous and may lead to an appreciable error in the computed values of E and τ_0. As such, this method can only be used to give a rough estimate of E and τ_0. These values for the series of phosphors are shown in Table 1.

The Bucci plot method yields better results, because it makes use of the whole experimental curve. The low temperature er of the peak and the high temperature end of peak were extrapolated to meet the abscissa. A typical thermally stimulated

Table 1. Evaluated values of activation energy/trap depth (E), τ_0 and attempt to escape frequency by Garlick-Gibson method.

Sl No	Sample No	Activator concentration	Trap depth (ev)	τ_0 sec	Attempt to escape frequency
1	MST1	0.01 mole%	1.511	3.810×10^{-15}	2.62×10^{14}
2	MST2	0 07 mole%	1.311	6.689×10^{-13}	1.494×10^{12}
3	MST3	0 15 mole%	1 420	1.920×10^{-14}	5.211×10^{13}
4	MST4	0.47 mole%	1 300	6.698×10^{-13}	1.497×10^{12}
5	MST5	0 79 mole%	1.512	1.800×10^{-15}	5.55×10^{14}
6	MST6	1.10 mole%	1.500	1.830×10^{-15}	3.02×10^{14}

conductivity curve is shown in Figure 1 (exposed to γ -ray = 1 16C/kg) All samples show only one peak. The integral in the numerator was calculated graphically from the TSC peak. The values of the areas below the TSC peaks and τ are calculated

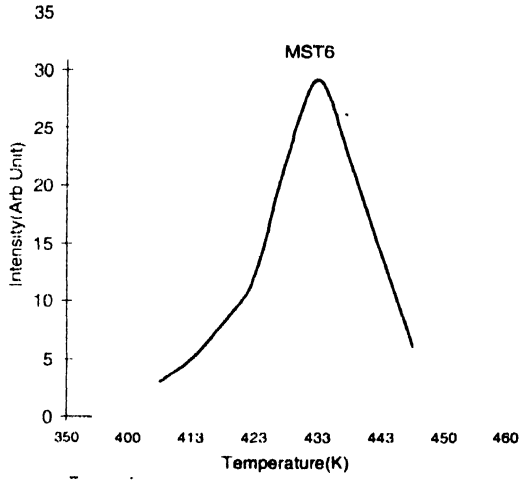

Figure 1. Thermally stimulated current *v/s* temperature

and the plot of ln τ *vs* $1/T$ for the peak of Figure 1 is shown in Figure 2. The slope of this plot yields E/k and intercept on the ln τ axis gives ln τ_0. Values of E and τ_0 calculated in this way for the series of phosphors are given in Table 2.

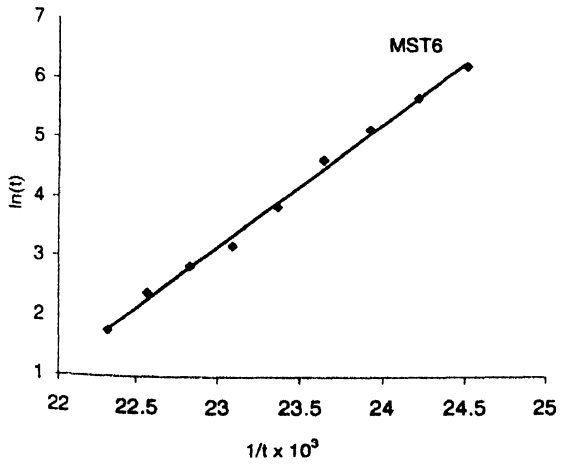

Figure 2. Values of τ at different temperatures.

Table 2. Evaluated values of activation energy/trap depth (E), τ_0 and attempt to escape frequency by Bucci plot method

Sl. No	Sample No.	Activator concentration	Trap depth (ev)	τ_0 sec	Attempt to escape frequency
1.	MST1	0.01 mole%	1.601	$2\,644\times10^{-17}$	$3\,782\times10^{16}$
2	MST2	0.07 mole%	1 570	$3\,240\times10^{-16}$	$3\,086\times10^{15}$
3.	MST3	0 15 mole%	1 450	$1\,160\times10^{-14}$	$8\,620\times10^{13}$
4	MST4	0 47 mole%	1 490	$3\,590\times10^{-15}$	$2\,785\times10^{14}$
5	MST5	0 79 mole%	1.530	$1\,290\times10^{-15}$	$7\,751\times10^{14}$
6	MST6	1.10 mole%	1 570	3.240×10^{-16}	3.086×10^{15}

Cowell and Woods method described in theory was then applied to the same TSC curve using the value of E from Bucci plot method and following the procedure described earlier. If the theoretical curve is found to be above the experimental one in the low temperature region, then a higher value of E is chosen and the process repeated. The value corresponding to the best fit is taken to be the correct value. The values of E, and τ_0, are reported in Table 3.

Table 3. Evaluated values of activation energy/trap depth (E), τ_0 and attempt to escape frequency using Cowell -Woods method

Sl No.	Sample No.	Activator concentration	Trap depth (ev)	τ_0 sec.	Attempt to escape frequency
1	MST1	0 01 mole%	1 584	$2\,150\times10^{-16}$	$4\,651\times10^{15}$
2.	MST2	0 07 mole%	1 545	$6\,340\times10^{-16}$	$1\,577\times10^{15}$
3.	MST3	0 15 mole%	1.452	$8\,340\times10^{-15}$	$1\,199\times10^{14}$
4.	MST4	0 47 mole%	1.586	2.160×10^{-16}	4.629×10^{15}
5.	MST5	0 79 mole%	1.500	$2\,270\times10^{-15}$	$4\,405\times10^{14}$
6.	MST6	1.10 mole%	1 586	2.160×10^{-16}	$4\,629\times10^{15}$

The following are the main conclusions drawn on the basis of qualitative analysis of (TSC) curves :

(i) The thermally stimulated conductivity at room temperature is found to decrease with the increase in activator concentration in the beginning while further with increase in concentration, it starts to increase with a peak temperature in the range of 419.0 K to 433.0 K. It is minimum for sample No. MST3 having activator concentration of 0.15 mol percent of calcium sulphate.

(ii) The values of the 'attempt to escape frequency' were found to be different for samples MST1 to MST6. This is the reciprocal of lifetime of an electron at a particular trap at a very high temperature. The substances ate supposed to be in the atomic state at this temperature. This lifetime comes out to be in the range 10^{-13} to 10^{-17} sec. An attempt to escape frequency factor in the range 10^{12} to 10^{16}. This factor was taken constant by the workers following the methods of Gross-Weiner

[13], Garlick-Gibson [3] and Randall-Wilkins [2]. This factor was assumed as constant by many research workers [12-15] in TSL and TSC measurements. This is the most important conclusion of this work and claims superiority of Bucci-Fischi and Cowell-Woods curve fitting technique over others, such as Gross-Weiner, Garlick-Gibson and Randall-Wilkins technique.

(iii) During γ -ray irradiation, holes are trapped at Ce^{3+} as well as at other site and at some Ce^{3+} sites. Formation of Ce^{4+} is a well-known mechanism of Ce^{3+} ions during γ or X- ray irradiation [17]. On heating, thermally released holes from Ce^{4+} site recombine with the electrons at unspecified sites. γ -ray induced oxidation of Ce^{3+} ions, viz., $Ce^{3+} \rightarrow Ce^{4+} + e^-$ shows the hole trap production. The Ce^{3+} ions exhibits, 4+ valence state after emission of electron in the 4*f* empty shell of electronic configuration of Ce ion. The higher TSC peak temperature of CaS:Ce indicates that the thermal activation energy of holes from Ce^{4+} sites is higher than that of the host lattice-related sulphide radicals. On the contrary, 2+ valance state could also be stable in the Ca^{2+} sub-lattice. Townsend and White [16] have, however, recently commented that the $RE^{3+} - RE^{2+}$ redox model in $CaSO_4$: RE has a conceptual problem since the hole not only captures but also stimulates the RE^{3+} luminescence.

(iv) The TSC peak is observed after heating the phosphors excited by γ -rays, resulting in recombination of charge carriers. Different impurity concentrations activated in CaS lattice, produced different energy level traps and the released electrons from traps recombine with holes at corresponding temperature and appeared in TSC peak.

(v) Many workers [9-13] calculated the trap depths with UV irradiated alkaline earth sulphide phosphors. They observed the values to be between 0.64 to 0.9 eV. But in our case, trap depths vary between 1.3 to 1.6 eV, which may be due to the use of γ -ray irradiated sample in place of UV irradiation. γ -ray radiation is found to increase high energy trap depths and during heating deeper traps are release at high energy level. Therefore, the value of trap depths is high as compared to UV irradiation.

(vi) The results obtained in the present study are associated with the γ -ray irradiation. Therefore, it is apparent that this particular group of traps is characteristic of the crystalline imperfections in the host lattice itself.

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